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Friction between single-grain $Al_{70}Pd_{21}Mn_9$ quasicrystal surfaces

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Abstract

An UHV tribometer was used to make measurements of friction between the five-fold surfaces of two single-grain $Al_{70}Pd_{21}Mn_9$ quasicrystals. The surfaces of these quasicrystal samples were either truly clean or modified by controlled adsorption of desired species. The results of many (~ 200) single-pass friction measurements using clean quasicrystal surfaces indicate that the average static friction coefficient is $\mu_s = 0.60 \pm 0.08$. The friction coefficient of the perfectly clean quasicrystal surfaces is lower than those reported for the perfectly clean surfaces of many pure metals but is higher than those measured on quasicrystal surfaces exposed to air. Under shear the quasicrystal surfaces slide over one another without exhibiting stick-slip behavior or adhesion. This behavior differs from clean metal surfaces that often exhibit adhesion after being brought into contact in ultra-high vacuum. Studies were performed to determine the effects of surface oxidation, surface structure and surface composition on quasicrystal friction. During the early stages of oxidation the static friction coefficient decreased to a limit of $\mu_s = 0.35 \pm 0.05$. More subtle changes to the quasicrystal surfaces such as adsorption of sulfur or formation of a thin Al–Pd–Mn alloy of CsCl structure produced no significant changes in the static friction coefficient.

Keywords: Adhesion; Alloys; Friction; Oxide; Quasicrystalline interfaces; Quasicrystals; Tribology

1. Introduction

Since the discovery of quasicrystals by Shechtman et al. in 1982 [1,2], there have been many studies of the physical properties and potential applications of these intriguing materials [3–9]. Quasicrystals are materials that possess long-range order without having the translational periodicity normally associated with ordered crystalline solids. Since their initial discovery, a variety of stable and metastable quasicrystalline materials have been made [10]. Most quasicrystals are ternary or higher order alloys of common metallic elements. Recent success in preparing single grain quasicrystals (1 cm × 1 cm) large enough for surface analysis by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) has enabled studies of the surface properties of quasicrystalline materials [11–15].

Quasicrystals have been shown to possess high hardness and high wear resistance [3,5–9]. Materials with these properties are also known to have low coefficients of friction and there are a number of measurements of friction between quasicrystal surfaces that have yielded low coefficients

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of friction [3,5–9,16–18]. Since these measurements have been performed in air, the surfaces are undoubtedly modified by the presence of adsorbed species or oxide films and may not reflect the properties of the truly clean surface. At a given load the true contact area between two surfaces of a hard material is smaller than that between surfaces of a soft material [16]. Since friction is a function of the true contact area between sliding solid surfaces, the surfaces of hard materials modified by adsorbed films of low shear strength will exhibit low friction. Whether the low friction exhibited by quasicrystals originates from their unique structural properties or high hardness poses a fundamentally important question and one whose answer may be of great significance for their future use in engineering applications.

All prior studies of the frictional properties of quasicrystals or quasicrystal coatings have been performed in air or under conditions where it is impossible to characterize the surface composition [3,5–9]. In scratch tests, Dubois et al. reported an average friction coefficient of ~ 0.20 at a constant load of 20 N for $Al_{65}Cu_{20}Fe_{15}$, $Al_{64}Cu_{18}Fe_8Cr_8$ and $Al_{67}Cu_9Fe_{10.5}Cr_{10.5}Si_3$ quasicrystal coatings using an AISI 52100 steel slider, and an average friction coefficient of ~ 0.05 with a diamond slider [3,5,7]. On $Al_xCu_yM_z$ (M = Fe, Fe–Cr, Fe–Cr–Si) and $Al_{59}Cu_{25.5}Fe_{12.5}B_3$ quasicrystals, the friction coefficient ranges from 0.06 to 0.17 using diamond, tungsten carbide, and AISI 52100 steel sliders [3,8,9].

One of the most intriguing issues of the tribology of quasicrystal surfaces is the origin of the low friction coefficients measured on their surfaces. Are the low friction coefficients a result of their unique structure? Do they reflect a property of the quasicrystal surfaces themselves or that of a surfaces modified by oxidation and the presence of airborne contaminants? In an effort to address these questions the experiments reported in this paper used single grain samples of $Al_{70}Pd_{21}Mn_9$ quasicrystal and studied their frictional properties in a controlled ultra-high vacuum (UHV) environment. The surfaces of these samples were prepared to be either truly clean or were modified by controlled adsorption of desired species. The ability to make friction measurements on surfaces prepared under UHV conditions has allowed us to study in detail the effects of surface modifications such as oxidation on friction between quasicrystals. The results of this work have shown that the friction between perfectly clean quasicrystal surfaces is certainly higher than that observed for air exposed surfaces, however, it is lowered by controlled oxidation.

2. Experimental

All experiments were performed in a stainless steel ultrahigh vacuum chamber with a base pressure below 1.0×10^{-10} Torr. The chamber is equipped with a four-grid retarding field analyzer (RFA) for LEED and AES; a quadrupole mass spectrometer; an Ar^+ ion sputter gun for cleaning of the quasicrystal surfaces; leak valves to introduce gases into the chamber; and an UHV tribometer to measure shear and normal forces between pairs of single crystal surfaces.

Two single-grain $Al_{70}Pd_{21}Mn_9$ quasicrystals of ~ 1 cm $\times$ 1 cm $\times$ 2 mm dimensions were mechanically polished to a mirror finish with 0.25 μm diamond paste. The quasicrystal boule from which the samples were cut consisted of several single grain quasicrystals and was grown at the Materials Processing Center of Ames Laboratory at Iowa State University using the Bridgman method [13]. The surface composition has been determined previously by both AES and X-ray photoelectron spectroscopy (XPS), and the bulk composition has been determined by inductively coupled plasma mass spectrometry (ICP-MS) [14]. Since quasicrystals are poor electrical conductors, the samples cannot be spot-welded directly to the manipulator. Instead, the samples were held against a Ta plate by Pd/Ag leaf springs spot-welded to the Ta plate. The plate was then spot-welded between two tantalum wires on a sample holder that was mounted at the end of a manipulator. The manipulator allows a wide range of motion in the x, y and z (vertical) directions as well as rotation about the vertical axis of the chamber. The sample could be heated resistively to $T > 800$ K and cooled to ~ 95 K through mechanical contact of the sample holder with a liquid nitrogen reservoir. The temperature of the quasicrystal was measured with a chromel–alumel thermocouple junction spot-welded to the back of the Ta plate. The quasicrystal on the manipulator was polished with slight spherical curvature (radius ~13 cm) to avoid edge contact with the second (flat) quasicrystal during friction measurements.

In addition to the curved quasicrystal sample mounted on the UHV manipulator, a flat quasicrystal was mounted on a UHV tribometer (force transducer) that allowed the simultaneous measurement of both shear and normal forces when the two were brought into contact with and sheared relative to one another [19]. The flat sample on the tribometer was held by Pd/Ag leaf springs to a Ta plate attached to a copper frame. The frame is clamped to a copper–beryllium sheet spring that deflects during friction measurements. A filament located behind the sample on the tribometer allowed heating by electron bombardment to $T>800$ K, and a liquid nitrogen reservoir allowed cooling to ~120 K. The temperature was measured with a chromel–alumel thermocouple junction spot-welded to the Ta plate near the edge of the sample. The contact between the spherically curved sample on the manipulator and the flat surface on the force transducer creates a pin-on-disk geometry for measurement of friction between the two. A detailed description of the UHV tribometer has been published elsewhere [19].

The response of the tribometer was calibrated while it was outside the UHV chamber by using objects ranging in weight (force under gravity = 2–250 mN). Both normal and shear responses (measured separately) were observed to be linear in the applied force over the calibration range. Within the chamber, the samples were aligned optically to ensure that their normals were parallel and that the sliding motion of the manipulator quasicrystal was parallel to the surface of the tribometer sample. Once the samples were aligned, they were brought into contact under the desired normal force ($F_N=5$–100 mN) and sheared relative to one another at a constant sliding speed ($v_{shear}=$ 1–100 μm s^{-1}) using motorized micrometers. Both the normal and shear forces were measured simultaneously over the usual sliding distance of 400–600 μm. Unless otherwise specified, the usual shearing conditions were: load of $F_N \cong 35$ mN, sliding speed of $v_{shear}=20$ μm s^{-1} and temperature of $T \cong 300$ K. A set of at least 12 single pass friction measurements was performed in each experiment. Between each single-pass measurement, the curved sample on the manipulator was rotated (~ ±1.5° from normal) and moved vertically to ensure that contact occurred at different points on the surfaces.

After any exposure to atmosphere, the sample surfaces were cleaned in vacuum by multiple cycles of 1 keV Ar^+ bombardment followed by annealing for 30 min. Initially the annealing temperature was increased in increments of 50 K from 450 to 850 K. The final step of the cleaning process consisted of repeated cycles of ion bombardment at room temperature for 30 min followed by annealing at 870 K for 2 h until the coverages of oxygen and other contaminants were reduced to the noise level of AES. Multiple cycles of 2 keV Ar^+ bombardment while annealing at 870 K for 30 min have been found to be another effective cleaning method. A sharp five-fold symmetric LEED pattern with secondary diffraction spots was observed after the samples had been cleaned properly.

In order to modify their surfaces the quasicrystals were exposed to extra dry oxygen (Matheson Gas Products), H_2S (Matheson, CP grade) or purified H_2O by back filling the chamber with vapor or gas. Exposures are reported in units of Langmuir (10^{-6} Torr s^{-1}) with the pressure uncorrected for ion gauge sensitivity. The effects of surface modification were determined by making a set of friction measurements (12–15 single pass measurements) using increasing adsorbate coverages until saturation coverage had been reached. The cleaning procedures described above were applied after each surface modification.

3. Results and discussion

3.1. *Frictional behavior of clean quasicrystal surfaces*

In order to study the intrinsic frictional properties of the five-fold surfaces of the $Al_{70}Pd_{21}Mn_9$ quasicrystals, numerous friction measurements were made using atomically clean quasicrystal surfaces. Once cleaned the sample surfaces exhibited sharp LEED patterns. The five-fold rotational symmetry of the flat quasicrystal surface is evident in the LEED pattern illustrated in Fig. 1. A similar LEED pattern was observed from the surface of the sample mounted to the manipulator except that the diffraction spots were broader due to its slight spherical curvature. The diffraction patterns were visible using electrons in the energy range of

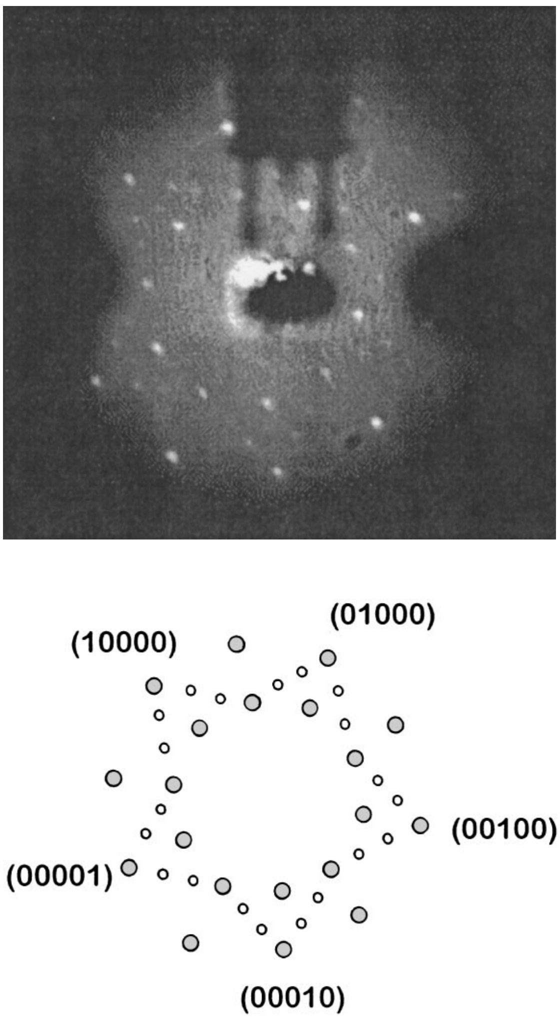

Fig. 1. LEED pattern of the clean five-fold quasicrystal surface at $T = 100$ K with an incident electron beam at 70 eV energy along the surface normal (top). A schematic diagram showing the five-fold rotational symmetry (bottom).

50–100 eV. The secondary LEED spots were observed when the sample surfaces were atomically clean but disappeared after background oxygen exposures of only 10 L at room temperature. The disappearance of the secondary diffraction spots as a result of low levels of surface contamination has been reported elsewhere [12].

Auger electron spectra were used to determine surface composition during cleaning and following surface modification. Spectra of the quasicrystal samples prior to cleaning showed that the major contaminants were: C (272 eV), O (510 eV), S (152 eV) and Cl (181 eV). In addition, the Al peak was observed at 55 eV indicating the presence of Al_2O_3 rather than metallic Al^0 (AES peak at 68 eV) [20]. The Pd (330 eV) and Mn (589 eV) peaks were not observed prior to cleaning. The Auger spectrum of the quasicrystal surface after extensive cleaning (Fig. 2) shows that the signals from oxygen and other airborne contaminants were reduced to below the noise level. Only peaks assigned to Al^0 (68 eV), Pd (330 eV) and Mn (589 eV) were detected indicating that the quasicrystal surfaces were clean.

Numerous friction measurements were made using the clean quasicrystals in UHV after the sample surfaces had been cleaned as determined by both the LEED and AES. Three randomly selected plots of shear and normal forces between the two surfaces measured as a function of time during sliding are shown in Fig. 3. Throughout this paper we have reported values of the static friction coefficient (μ_s), defined as the shear force needed to initiate sliding divided by the normal force, as extracted from each friction measurement. Other definitions of μ such as the dynamic friction coefficient (μ_d), defined as the ratio of the steady-state shear force to the normal force, could have been reported but would not change the overall conclusions of this work. In this paper, values of μ_s will be used for comparison with other friction measurements between clean metal surfaces.

The procedure used to make the friction measurement involves several steps. Referring to Fig. 3, one can observe the response of the tribometer signal to these various steps. At point A, the two sample surfaces were out of contact. At point B, the manipulator sample was brought into contact

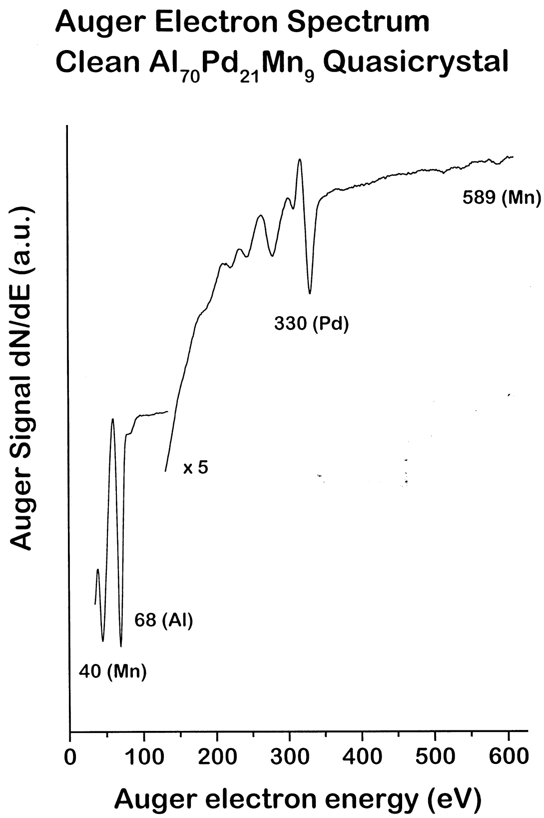

Fig. 2. Auger electron spectrum of the clean $Al_{70}Pd_{21}Mn_9$ quasicrystal surface. Only peaks of Al (68 eV), Pd (330 eV) and Mn (40 eV, 589 eV) are detected.

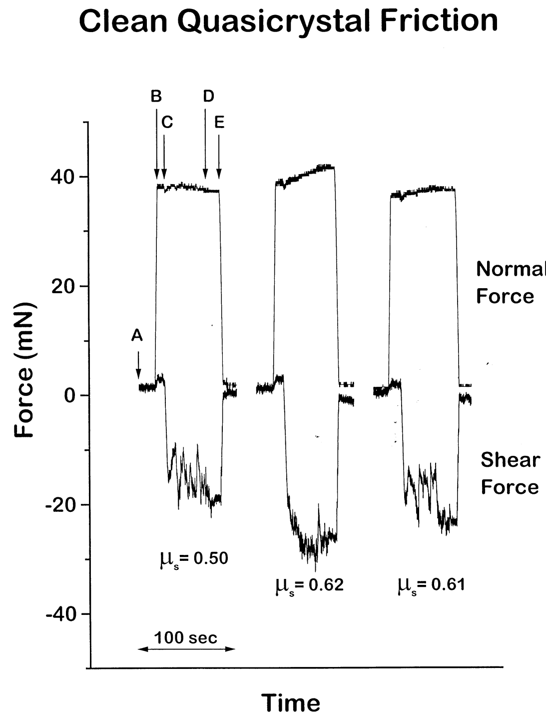

Fig. 3. Three friction measurements made between clean $Al_{70}Pd_{21}Mn_9$ quasicrystal surfaces. The upper trace is a plot of the normal force (F_N), while the lower trace is a plot of the shear force (F_S). Sliding conditions: $F_N \cong 35$ mN, $v_{shear} =$ 20 μm s^{-1}, $T_c \cong 3$–6 s, $T \cong 300$ K. No adhesion or stick-slip features were observed.

with the tribometer sample as indicated by the increase in the normal force. The two samples were held in contact for a brief period (3–6 s) before shearing began at point C. At a constant load and sliding speed, the shear force increased as shearing began and then reached a roughly constant value as one surface slid over the other. At point D, the shearing stopped, and the samples were then separated at point E with the normal and shear forces returning to zero. Adhesion between the surfaces following sliding would have been observed as a negative normal force between the two as they were being separated. Although this has been observed between clean Cu(111) surfaces it was not observed between the quasicrystal surfaces.

One of the parameters which may influence the friction measurements is the crystallographic orientation of the quasicrystal surfaces with respect to one another. There are suggestions in the literature that the orientation of crystalline surfaces affects the friction coefficient. McGuiggan and Israelachivili have shown that the interaction between two mica surfaces in liquids depends on the orientation of the surface lattices. This effect is a function of the gap between the mica surfaces, and the lattice orientation effects can extend to a gap thickness equivalent to four molecular layers of liquid [21]. Friction measurements made between clean Cu(111) surfaces in our laboratory have given very different values of the static friction coefficients after the crystals have been rotated and remounted [22–24]. As determined by LEED patterns obtained from both the manipulator and the tribometer quasicrystal sample surfaces, the friction results reported here were made with an $\sim 10°$ lattice mismatch of the five-fold axes with respect to one another as seen in Fig. 4. The shearing direction is indicated in Fig. 4 with the corresponding lattice mismatch. A detailed study of the consequences of this misorientation has yet to be performed.

The results of many (~ 200) single-pass friction measurements using clean quasicrystal surfaces indicate that the average static friction coefficient is $\mu_s = 0.60 \pm 0.08$. No stick-slip behavior or adhesion was observed between clean quasicrystal surfaces. The frictional properties of quasicrystal surfaces or quasicrystal coatings sliding against various materials have been measured in other laboratories [3,5,7–9]. On $Al_xCu_yM_z$ (M = Fe, Fe–Cr, Fe–Cr–Si) and $Al_{59}Cu_{25.5}Fe_{12.5}B_3$ quasicrystals, the friction coefficient ranges from 0.06 to 0.17 using diamond, tungsten carbide and AISI 52100 steel sliders under a constant load of 20 N [3,8,9]. In scratch tests, Dubois et al. reported an average friction coefficient of ~ 0.20 for $Al_{65}Cu_{20}Fe_{15}$, $Al_{64}Cu_{18}Fe_8Cr_8$ and $Al_{67}Cu_9Fe_{10.5}Cr_{10.5}Si_3$ quasicrystal coatings using an AISI 52100 steel slider, and an average friction coefficient of ~ 0.05 with a diamond slider [3,5,7]. The major distinction between the measurements made in other laboratories and our measurements is that we were able to shear two atomically clean quasicrystal surfaces in UHV. One obvious source of difference between other friction measurements and ours is the presence of surface contamination. Our measurements of friction between quasicrystal surfaces in air prior to any cleaning yielded an average static friction coefficient of $\mu_s = 0.11 \pm 0.02$ which is, of course much lower than that of the clean surfaces. Auger spectra of the air exposed surface indicated the presence of air borne contaminants such as carbon, oxygen and sulfur on the surfaces. It appears that these surface contaminants are responsible for the low friction coefficients measured in air.

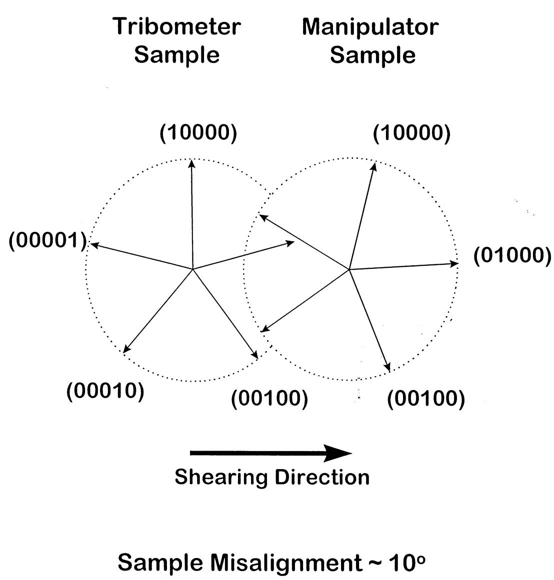

Fig. 4. Schematic diagram showing the lattice mismatch of the five-fold rotational symmetry axes of the manipulator and tribometer samples with the shearing direction indicated.

The coefficient of friction between the clean quasicrystal surfaces ($\mu_s = 0.60 \pm 0.08$) can be compared with friction coefficients measured between the surfaces of other materials that have been prepared and cleaned in UHV. Beginning with those measurements made in our laboratory using the same apparatus we can compare to the friction coefficients measured between pairs of Cu(111) surfaces ($\mu_s = 4.6 \pm 1.1$ [23]), Ni(100) surfaces ($\mu_s = 2.4 \pm 1.0$ [19]) and W(110) surfaces ($\mu_s = 0.65 \pm 0.08$ [25]). Clearly the only case in which the clean metal surfaces have friction coefficients comparable to those of the quasicrystals is in the case of tungsten which also happens to be the hardest. Although there are a number of measurements of friction made in UHV that have been reported in the literature, the majority tend to be between dissimilar materials or in some cases under conditions where it was not possible to clean and analyze both surfaces forming the sliding pair. In making comparisons to our measurements it seems most appropriate to limit ourselves to those measurements using pairs of identical surfaces. One example is a measurement of the friction between pairs of Fe surfaces. At the highest level of cleanliness that could be achieved the friction coefficient was in the range $\mu_s = 5$–6 [26]. Of those measurements which have been made using pairs of identical materials, there are some which show friction coefficients lower than those observed for the quasicrystals. The friction coefficients between pairs of single crystalline manganese–zinc ferrite were found to lie in the range $\mu_s = 0.2$–0.4 depending upon the relative orientations of the two crystalline surfaces [27].

One set of UHV friction measurements has been made using metallic alloys similar to the quasicrystalline alloys used in this work. These are a set of metallic glasses with compositions $Fe_{42}Co_{11}B_{46}Si$, $Fe_{48}B_{42}Si_4C_6$ and $Fe_{23}Ni_{21}Mo_4B_{55}$ having hardnesses in the range 10–10.5 GPa. These were cleaned in UHV to the point that total surface contamination by carbon and oxygen was on the order of 10–20 at%. Under these conditions the friction coefficients measured using an Al_2O_3 pin were in the range $\mu_s = 1.0$–1.5 [28,29].

3.2. Dependence of the static friction coefficient on shearing conditions

The sole purpose of studying the dependence of the static friction coefficient on shearing conditions such as load (F_N), sliding speed (v_{shear}), contact time (t_c) prior to sliding, and temperature (T) was to confirm that slight deviations of these parameters from one measurement to another did not influence the friction coefficient. Several sets of friction measurements were made between clean quasicrystal surfaces using various loads (10, 35 and 50 mN); sliding speeds (5, 20 and 70 μm s^{-1}); contact times (1, 5 and 10 s); and temperatures (~120 and ~300 K). A plot of the static friction coefficient as a function of shearing conditions is illustrated in Fig. 5. Clearly, there is no significant dependence of the static friction coefficient on any of these parameters in the ranges studied. The sliding conditions used for all other measurements ($F_N \cong 35$ mN, $v_{shear} = 20$ μm s^{-1}, $t_c \cong 3$–6 s, $T \cong 300$ K) are all within the ranges studied.

3.3. Friction between oxidized quasicrystal surfaces

A number of interesting questions can be posed concerning the low frictional properties of quasicrystalline surfaces. Is low friction a direct result of quasicrystallinity or of bulk mechanical properties? Does surface structure have an effect on friction? Do adsorbed species such as oxygen or sulfur influence friction? It seems clear that the presence of airborne contaminants will influence the friction of the quasicrystals, but to understand why it is necessary to study the effects of systematic modifications to their surfaces.

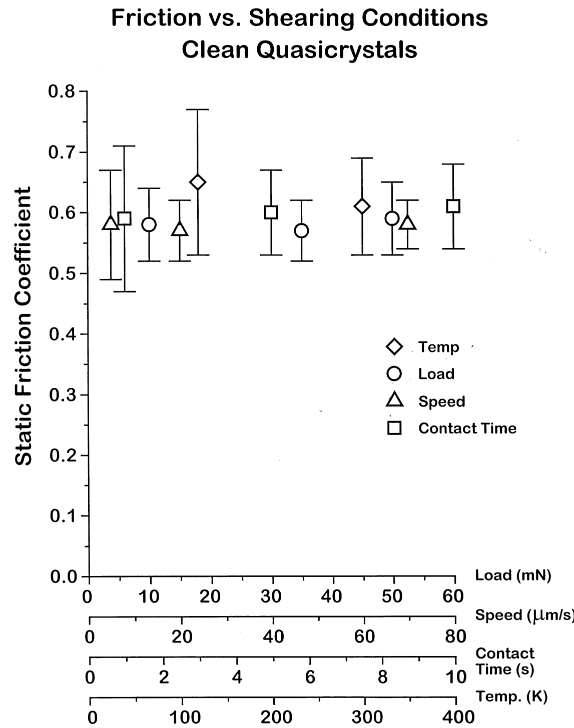

Fig. 5. Static friction coefficient as a function of sliding conditions (load, speed, contact time, and temperature). The normal sliding conditions ($F_N \cong 35$ mN, $v_{shear} = 20$ μm s^{-1}, $t_c \cong 3$–6 s, $T \cong 300$ K) are within the ranges studied.

In order to study the effects of quasicrystal surface composition on friction we have modified their surfaces by controlled oxidation. Two sets of friction measurements were made using oxidized quasicrystal surfaces. The first set used surfaces oxidized by increasing exposure to oxygen at room temperature. This treatment oxidized the near surface region of the quasicrystals. The second set of measurements differed in that the surfaces were first oxidized by exposure to O_2 and then by exposure to H_2O vapor. Oxidation with H_2O resulted in a much thicker oxide film [14]. Fig. 6 shows three Auger electron spectra of the quasi-

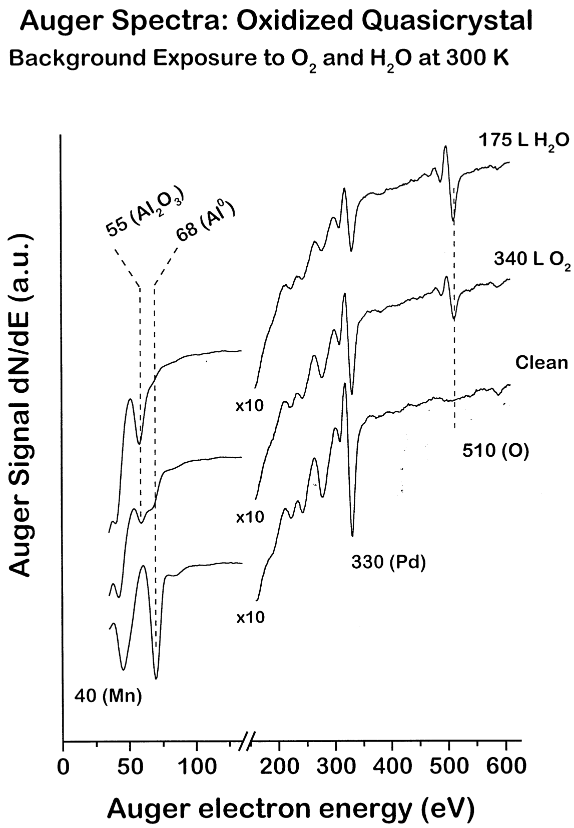

Fig. 6. Auger electron spectra of quasicrystal surface following oxidation. The emergence of the oxygen feature at 510 eV and the conversion of Al^0 (68 eV) to Al_2O_3 (55 eV) demonstrate that exposure to O_2 and H_2O caused oxidation. Oxidation of clean quasicrystal samples by O_2 exposures ($\sim$340 L) did not fully oxidize the surfaces as indicated by the middle Auger electron spectrum in which a shoulder at 68 eV (Al^0) was still detectable. Only with additional exposure to H_2O vapor ($\sim$175 L) did the Al^0 (68 eV) fully convert to Al_2O_3 (55 eV).

crystal surface following various oxidation treatments. The emergence of the oxygen feature at 510 eV and the conversion of Al^0 (68 eV) to Al_2O_3 (55 eV) demonstrate that exposure to O_2 and H_2O caused oxidation. Oxidation of clean quasicrystal samples by O_2 exposures ($\sim$340 L) did not fully oxidize the surfaces as indicated by the middle Auger electron spectrum in which a shoulder at 68 eV was still detectable revealing the presence of metallic Al^0 in the near surface region. Only with additional exposure to H_2O vapor ($\sim$175 L) did the Al^0 (68 eV) fully convert to Al_2O_3 (55 eV). The trend of decreasing Pd (330 eV) and increasing O (510 eV) Auger intensities with increasing oxidation observed in Fig. 5 can be attributed to increasing oxide thickness. Jenks et al. reported a similar observation and calculated an oxide thickness of 6 Å following saturation with O_2 in vacuum and an oxide thickness of 62 Å following exposure to humid air [14]. In Fig. 7, the absolute Auger intensity of the oxygen (510 eV) peak is plotted as a function of exposure to O_2 and H_2O. The oxygen and H_2O uptake curves indicate that saturation by O_2 occurred at an exposure of $\sim$300 L and that saturation by H_2O occurred at an exposure of >170 L.

The influence of surface oxidation on friction was explored by making a large number of friction measurements at all stages of oxidation. The results of friction measurements made between oxidized quasicrystal surfaces can be seen in Fig. 8. In the first set of measurements made during oxidation by O_2, the static friction coefficient decreased from $\mu_s = 0.60 \pm 0.08$ for the clean surfaces to $\mu_s = 0.44 \pm 0.04$ following a 310 L exposure to O_2. The lower limit of the static friction coefficient was reached after an exposure of 35 L coinciding with the point at which the LEED pattern disappeared. In the second set of friction measurements, the static friction coefficient reached a limit of $\mu_s = 0.37 \pm 0.08$ following oxidation by O_2 and a value of $\mu_s = 0.35 \pm 0.05$ following further oxidation by H_2O. The result indicates that the static friction coefficient is not influenced by oxide thickness beyond that produced by $\sim$35 L of oxygen exposure. The average static friction coefficient observed in this work is close to that of the friction studies of Blau on alumina (Al_2O_3) surfaces [30,31]. In those studies, a pin-on disk tribometer was used (Al_2O_3 on Al_2O_3) and measured friction coefficients in the range $\mu_s = 0.25$–0.42. A much earlier study of the friction between pairs of Al_2O_3 basal planes gave friction coefficients in the range $\mu_s = 0.15$–0.25 in air and $\mu_s = 0.5$–0.7 in UHV [32]. In none of these cases was it possible to analyze the Al_2O_3 surfaces for cleanliness, however, they do indicate numbers in the range of those that we have observed between the oxidized quasicrystals surfaces.

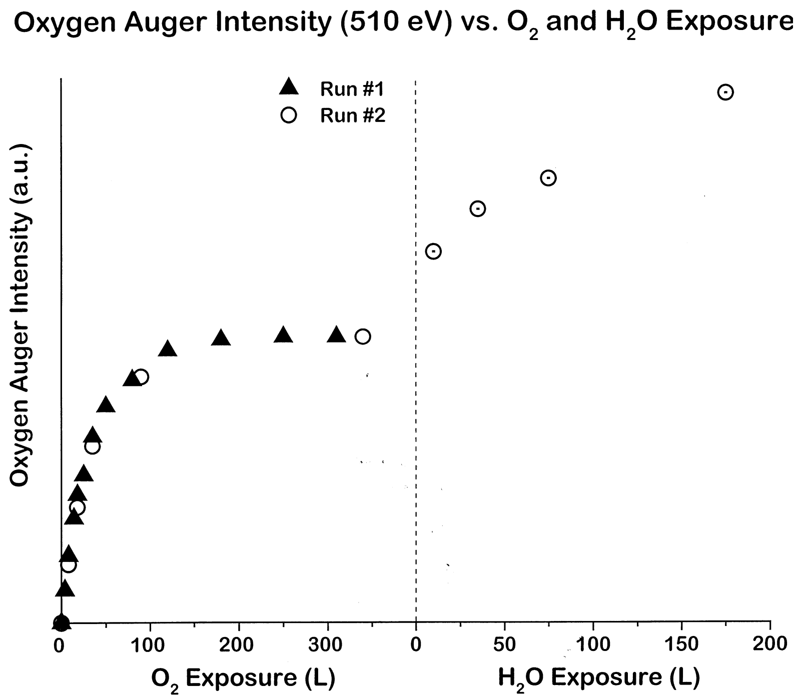

Fig. 7. Auger electron signal indicating uptake of oxygen by the quasicrystal surface during exposure to O_2 and then exposure to H_2O.

3.4. Friction between modified quasicrystal surfaces

In an effort to determine the factors that will influence the friction between quasicrystal surfaces in sliding contact, several modifications were made to the sample surfaces. It is clear from previously described results that the gross levels of contamination resulting from air exposure will reduce friction. Similarly, oxidation to produce thin (~ 6 Å) films of aluminum oxide will also lower the friction between these surfaces although not to the levels reached by surfaces contaminated by exposure to air. The final two modifications made in this study consist of the adsorption of a single monolayer of sulfur by dissociation of H_2S and the formation of a thin film of $Al_xPd_yMn_z$ alloy having a CsCl structure on the quasicrystal surface. The alloy film has a stoichiometry similar to that of the quasicrystal but with a periodic, non-quasicrystalline structure. These modifications are considered to be more 'subtle' than those produced by air contamination or oxidation.

Sulfur atoms are known to form ordered overlayers on many single crystal metal surfaces [33–37]. With the hope of observing an 'ordered' overlayer and new LEED pattern on the quasicrystal surface, sulfur was adsorbed on the quasicrystal surface (at 300 K) by introduction of H_2S into the chamber. The five-fold rotational LEED pattern disappeared after an exposure to H_2S of ~ 8 L at 300 K. Unfortunately, no new LEED pattern was observed at any exposure or sulfur coverage. The sulfur Auger peak at 152 eV clearly indicated adsorption of sulfur on the sample surface. Saturation coverage was reached following a ~ 14 L exposure to H_2S as indicated by the sulfur uptake curve (not shown). The Auger electron spectrum of the sulfided quasicrystal surface after an exposure to ~ 14 L of H_2S can be seen in Fig. 9. No serious effort has been made to determine the absolute coverage of the sulfur overlayer, however, the AES signal suggests that it is of the order of the saturation overlayers often produced by H_2S dissociation on single crystal metal surfaces. In

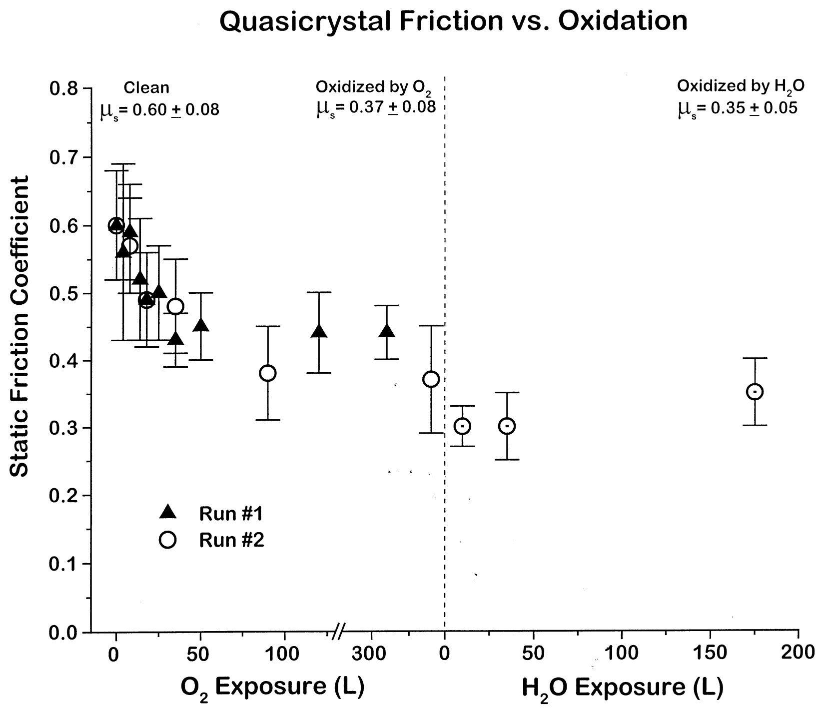

Fig. 8. Static friction coefficient between two quasicrystal surfaces modified by increasing exposure to O_2 and then H_2O. The static friction coefficient was lowered from $\mu_s = 0.60 \pm 0.08$ for the perfectly clean surfaces to $\mu_s = 0.35 \pm 0.05$ after complete oxidation. Error bars were calculated as the standard deviations in the results of at least 12 single-pass friction measurements. Two sets of friction measurements were made and are shown separately with open and filled symbols.

other words the coverage is $\theta_S < 10^{15}\ \mathrm{cm}^{-2}$ or equivalent to the fractional monolayers often observed. Following adsorption of a saturation sulfur coverage, friction measurements were made between the pair of sulfided quasicrystal surfaces. As shown in Fig. 10, no significant change in the static friction coefficient was seen between clean ($\mu_s = 0.60 \pm 0.08$) and sulfided quasicrystal surfaces ($\mu_s = 0.47 \pm 0.06$). This is consistent with previous observations of McFadden and Gellman who reported that saturated sulfur overlayers had no significant effect on the friction coefficient of Cu(111) surfaces in sliding contact [22,23].

In order to address the relationship between low friction and quasicrystallinity, friction measurements were made on clean 'pseudo-ten-fold' quasicrystal surfaces. Cycles of annealing the $Al_{70}Pd_{21}Mn_9$ sample at 650 K for 30 min generated a thin film alloy overlayer with two-fold rotational symmetry in five equivalent domains [38,39]. The apparent ten-fold rotational symmetry was observed by LEED. However, the diffraction spots were very broad, and therefore no LEED photographs were taken. A similar transition in surface structure was observed on a decagonal $Al_{70}Ni_{17}Co_{13}$ quasicrystal by Edagawa and Takeuchi who produced surfaces alloys exhibiting pseudo-five- and ten-fold rotational symmetries using different annealing treatments (923 K versus 1123 K) [40]. The transition to 'pseudo-ten-fold' rotational symmetry was also observed by Shen et al. on the $Al_xCu_yFe_z$ quasicrystal surface [38,39]. The surface alloys do not have the same stoichiometry as the bulk quasicrystals. As seen in Auger electron spectrum 'B' of Fig. 9, only Al^0 (68 eV), Pd (330 eV) and Mn (589 eV) were detected indicated that the pseudo-ten-fold surface was clean. However, the intensities of Pd and Al^0 peaks differ from those of the Auger spectrum of the clean five-fold quasicrystal surface illustrated in

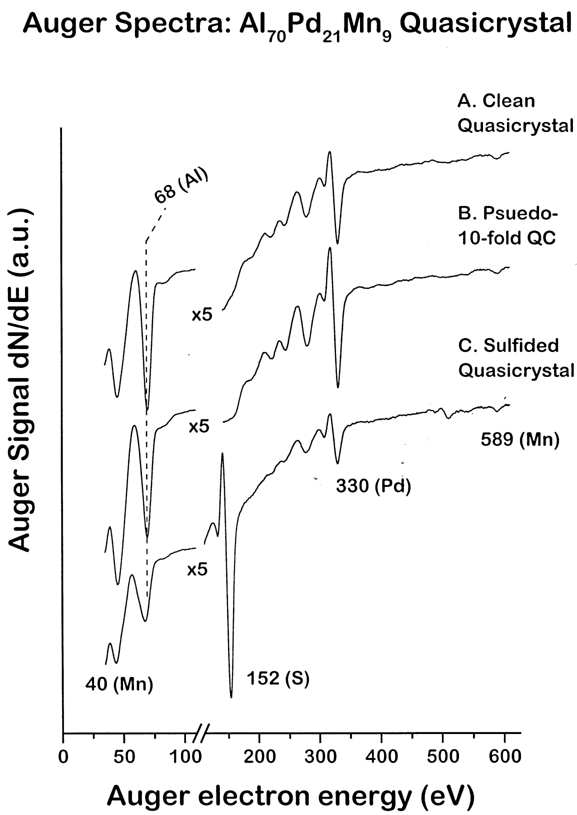

Fig. 9. Plots of Auger electron spectra of various modified quasicrystal surfaces. Spectrum A shows a clean quasicrystal surface. Spectrum B was obtained after the 'pseudo-ten-fold' LEED pattern was observed. The sulfur Auger peak at 152 eV of spectrum C indicates a sulfided quasicrystal surface.

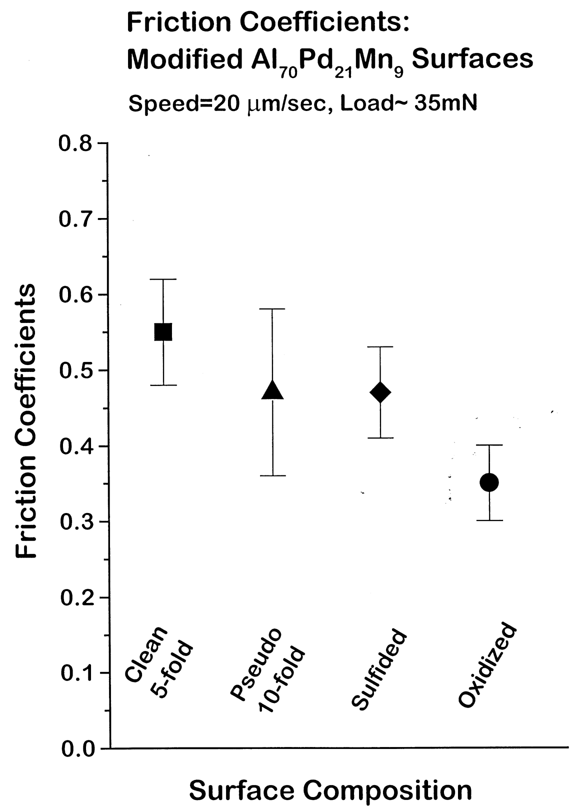

Fig. 10. Static friction coefficients of quasicrystal surfaces following various modifications. No significant change in friction coefficient was seen when sulfur was adsorbed or when surface structure was altered. Only with surface oxidation does the friction coefficient decrease.

spectrum 'A'. The 'pseudo-ten-fold' surface has been shown to be formed of a thin film alloy having a cubic CsCl structure [41]. This thin film alloy is Pd rich with respect to the quasicrystal and has a stoichiometry estimated at $Al_{63\pm3}Pd_{33\pm2}Mn_{4\pm2}$.

Friction measurements between the quasicrystal samples were made before and after the transition to 'pseudo-ten-fold' symmetry. As seen in Fig. 10, no significant change in static friction coefficient was observed when surface symmetry was altered. In this particular set of experiments a static friction coefficient of $\mu_s = 0.47 \pm 0.11$ was measured between 'pseudo-ten-fold' surfaces compared to $\mu_s = 0.60 \pm 0.08$ on clean five-fold quasicrystal surfaces. Clearly, these 'subtle' changes in the quasicrystal surfaces do not have any significant influence on their surface mechanical properties.

4. Conclusion

This paper reports the first results of friction measurements made using truly clean single-grain $Al_{70}Pd_{21}Mn_9$ quasicrystal surfaces in a highly controlled UHV environment. All previous friction measurements made on quasicrystal surfaces have been made in air and are therefore subject to possible effects of air borne contaminants rather than reflecting the true frictional behavior of quasicrystalline surfaces. The results of many (~200) single-pass friction measurements using clean quasicrystal surfaces indicate that the static friction coefficient is $\mu_s = 0.60 \pm 0.08$. No adhesion or stick-slip sliding behavior was seen between clean quasicrystal surfaces.

Measurements made under UHV conditions clearly reveal that the frictional properties of the quasicrystal surfaces are influenced by gross modifications to the surfaces such as those produced by air contamination or oxidation. The effect of surface oxidation on quasicrystal friction was examined in some detail. The results indicate that the static friction coefficient is dependent on surface oxidation of the quasicrystals decreasing to a limit of $\mu_s = 0.35 \pm 0.05$ in the early stages of oxidation. This number is still higher than the value of $\mu_s = 0.11 \pm 0.02$ that we have measured between air exposed surfaces. Oxidation alone does not seem to account for the low value of friction coefficients measured in air.

Subtle changes in the quasicrystal surface structure and composition were also made in order to determine their influence on friction. Alteration of the surface symmetry and structure by generation of an alloy overlayer with similar composition to a CsCl structure had no significant influence on the friction coefficient. Similarly, the adsorption of a submonolayer coverage of sulfur by dissociation of H_2S had no influence on the friction coefficient.

The results from friction measurements made using atomically clean quasicrystal surfaces confirm that quasicrystals possess low friction coefficients compared with those commonly reported between perfectly clean surfaces of pure metals. The only pure metal with comparable clean surface friction is tungsten. Whether the low friction exhibited by quasicrystals originates from their structural properties, high hardness or other properties poses a fundamentally important question whose answer may be of great significance for their future application.

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